

## Enhancing the Thermal Stability of Polythiophene:Fullerene Solar Cells by Decreasing Effective Polymer Regioregularity

Kevin Sivula, Christine K. Luscombe, Barry C. Thompson, and Jean M. J. Fréchet\*

*Departments of Chemistry and Chemical Engineering, University of California, Berkeley, 718 Latimer Hall, Berkeley, California 94720-1460, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

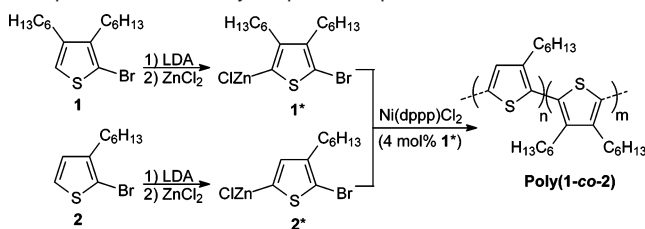
Received June 22, 2006; E-mail: frechet@berkeley.edu

Thin-film photovoltaics made from a bulk heterojunction (BHJ) between poly(3-hexylthiophene) (P3HT) and the fullerene derivative [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) have emerged as the most promising organic solar cell system.<sup>1,2</sup> The morphology of the active layer in these devices has garnered particular interest because electron transfer from the donating polymer to the accepting fullerene<sup>3</sup> occurs over a distance of ca. 10 nm, suggesting that an interpenetrating network of that length scale is necessary for maximum device performance. A thermal annealing step, above the *T<sub>g</sub>* of the polymer, is necessary to increase its crystallinity in order to improve its electrical properties, but thermal annealing also drives the phase segregation of P3HT and PCBM.<sup>4,5</sup> Phase segregation destroys the BHJ, thereby reducing device performance,<sup>5</sup> and thus, optimal thermal annealing conditions are required to delicately balance increasing P3HT crystallinity while minimizing phase segregation of the active components. The recent discovery of conditions to attain a thermally stable interpenetrating network of P3HT and PCBM<sup>1</sup> has led to devices with simulated solar power (AM 1.5G) conversion efficiencies in the range of 4–5% using a 90–93% regioregular (RR) P3HT from a commercial source.<sup>6</sup>

Much effort has been devoted to understanding how the properties of P3HT affect its electronic characteristics. Increasing the molecular weight (MW) of the polymer has been shown to enhance the charge carrier mobility of pristine P3HT in both the field effect<sup>7</sup> and space-charge limited<sup>8</sup> regimes. Regioregularity has also been shown to affect charge carrier mobility in polythiophene thin films.<sup>9</sup> As expected, P3HT with both increased molecular weight<sup>10</sup> and regioregularity<sup>11</sup> enhances performance in P3HT:PCBM photovoltaic devices. While tuning the MW of P3HT is easily achieved through modulating the polymerization conditions, and methods of producing essentially 100% RR–P3HT have been reported,<sup>12,13</sup> a straightforward route to adjusting the regioregularity of P3HT has been elusive. We now present a new method to tune the regioregularity of P3HT and report that, surprisingly, a small decrease in the effective regioregularity of P3HT appears to confer more thermal stability to the BHJ of P3HT and PCBM with implications on long-term performance.

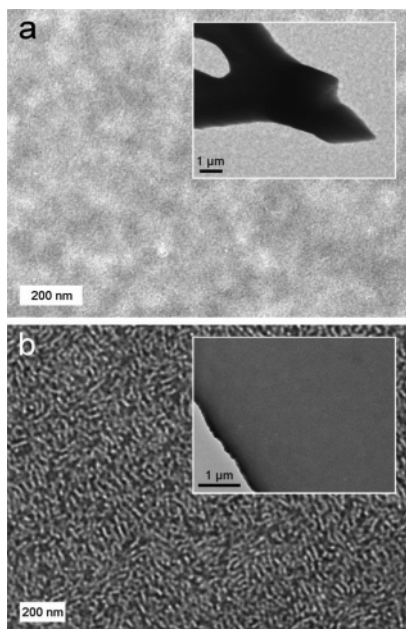
To reduce the effective regioregularity of P3HT, we began with the McCullough method, which is known to produce highly RR–P3HT,<sup>14</sup> while also randomly incorporating a thiophene monomer with *n*-hexyl chains at both the 3 and 4 positions. Monomers **1** and **2** (Scheme 1) were prepared using standard procedures (see Supporting Information). The activated zinc species **1\*** and **2\*** were prepared in separate flasks at known concentrations before **1\*** was combined with **2\*** *in situ* in the ratio of 1:24 prior to the addition of 1 mol % of nickel catalyst to initiate polymerization. A control sample of RR–P3HT was synthesized using the same procedure, and the molecular weights of the polymers were found to be similar (GPC *M<sub>n</sub>* = 22 and 28 kDa for poly(**1-co-2**) and the control P3HT,

**Scheme 1.** Synthetic Route for Lowering Regioregularity by the Incorporation of a Dihexylthiophene Repeat Unit

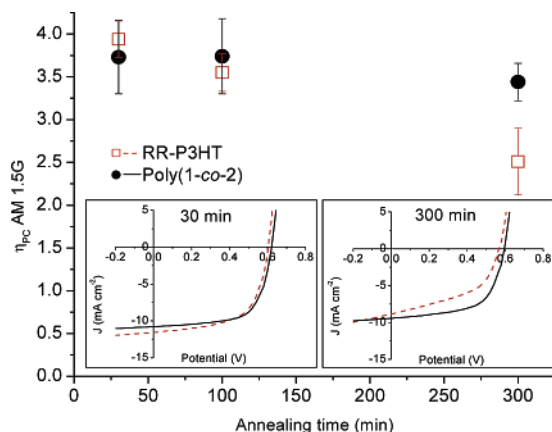


respectively). MALDI-TOF MS analysis of the purified copolymer confirms the incorporation of monomer **1**, and <sup>1</sup>H NMR characterization (Figures S1 and S2) allows the comparison of regioregularities. Regioregularity is typically calculated by comparing the integrated peaks corresponding to the α-methylene protons on the hexyl chains in head-to-tail (HT) versus head-to-head (HH) linkages,<sup>12</sup> δ2.78 and δ2.54, respectively. This gives >96% HT for the control P3HT. The same analysis gives an effective regioregularity of 91% for poly(**1-co-2**), which is lower, as expected, since the incorporation of monomer **1** increases the content of non-HT linkages in the copolymer.

To investigate the BHJ morphology, thin films of poly(**1-co-2**), or the control P3HT, and PCBM (1:1 by weight) were spin-cast from chlorobenzene onto a freshly cleaved single-crystal NaCl substrate and annealed, with the top unconfined, at typical device fabrication conditions (150 °C for 30 min). The films were then removed by floating on water and placed on TEM grids for analysis. The resulting micrographs (Figure 1) show the typical large-scale phase segregation of the PCBM from the P3HT in the BHJ prepared with the control polymer, along with no obvious features upon close inspection of the regions free from PCBM (Figure 1a). In contrast, blends made with poly(**1-co-2**) produced a thermally stable interpenetrating network with vermicular features on the order of 20 nm in width (Figure 1b). This morphology was also observed in BHJs prepared using the commercially available polymer.<sup>1</sup> We suggest that the high driving force for crystallization of the RR–P3HT control material initiates the phase segregation of the BHJ by the exclusion of PCBM from the ordered P3HT domains. The stark contrast in the ability of poly(**1-co-2**) to retain a bicontinuous morphology relative to RR–P3HT is consistent with our claim that introducing disorder, in the form of the dihexyl-functionalized monomer **1**, serves to attenuate the driving force for crystallization and facilitates the retention of a thermally stable BHJ during annealing. Unoptimized photovoltaic devices fabricated with the control polymer or poly(**1-co-2**) and PCBM (1:1 by weight) support this conjecture (Figure 2; note that *each* data point is the average for eight devices). While 30 min of annealing after cathode deposition produced devices with similar power conversion efficiencies (up to η<sub>PC</sub> = 4.3 and 4.4% for the control and poly(**1-**



**Figure 1.** Transmission electron micrographs of annealed BHJ thin films containing 1:1 by weight RR-P3HT:PCBM (a) and poly(1-co-2):PCBM (b). An interpenetrating network of polymer and fullerene is observed with poly(1-co-2) (b), while no obvious features are seen in the polymer region of the control case (a). The insets show a wider view of the films and the micron-scale phase segregation of PCBM (dark region) from the RR-P3HT in the control case. No micron-scale features are observed when poly(1-co-2) is used in the BHJ. The film edge is shown to confirm focus in the inset of (b).



**Figure 2.** Performance of photovoltaic devices fabricated with the control RR-P3HT or poly(1-co-2). The eight-device average power conversion efficiency ( $\eta_{PC}$ ) at standard conditions as a function of annealing time at 150 °C and typical  $J$ - $V$  behavior (insets) observed after 30 and 300 min of annealing illustrate the difference between the materials. The error bars represent the 95% confidence interval of the average values.

co-2), respectively, at AM 1.5G, 100 mW cm<sup>-2</sup>, continued annealing of RR-P3HT devices causes a decrease in performance, and after 300 min at 150 °C, the average  $\eta_{PC}$  fell to 2.6%. Subjecting devices with a poly(1-co-2):PCBM active layer to the same extended annealing conditions does not strongly effect the average device performance, and the eight-device average  $\eta_{PC}$  remained at 3.5%. We observe comparable annealing behavior with the commercial P3HT (see Supporting Information). In addition, we note the decrease in device performance in the RR-P3HT devices, caused by phase segregation, occurs at longer times than for the TEM samples due to the confining effects of the Al cathode.<sup>5</sup>

Given that we have been able to obtain similar performance at short annealing times with both the control polymer and poly(1-

co-2), we can conclude that incorporation of a small amount of monomer **1** into P3HT does not significantly effect its electronic properties. Additionally, since we have observed identical device performance and stability for poly(1-co-2) and the commercially available material, which has a significantly higher  $M_n$ ,<sup>6</sup> it is unlikely that molecular weight plays a major role in forming a stable BHJ. However, because poly(1-co-2) and the commercial material have similar amounts of disorder (in the form of HH linkages), greater than the control RR-P3HT, we conclude this is an important aspect in forming a thermally stable BHJ with PCBM. Thus the 5% efficiency<sup>1</sup> obtained through rigorous optimization of devices prepared using commercial P3HT may be due to the fortuitous lower RR of that material,<sup>6</sup> which eliminates the concern of phase segregation. Obtaining a stable interpenetrating network of electron donor and electron acceptor is important for organic photovoltaics. Here we have seen that, while maximizing regioregularity in P3HT may provide the best electronic properties in the pristine material, the most stable photovoltaic performance is obtained with a polythiophene with a tuned regioregularity to control the BHJ morphology.

**Acknowledgment.** Financial support of this work by the Department of Energy (DE-AC03-76SF00098) is gratefully acknowledged. B.C.T. acknowledges funding from an ACS PRF postdoctoral AEF. We thank Prof. A. P. Alivisatos and his group for fabrication facilities and helpful discussion of this work.

**Supporting Information Available:** Complete synthetic procedures, characterization, and device fabrication methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.
- (2) (a) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864–868. (b) Reyes-Reyes, M.; Kim, K.; Carroll, D. L. *Appl. Phys. Lett.* **2005**, *87*, 083506.
- (3) (a) Markov, D. E.; Amsterdam, E.; Blom, P. W. M.; Sieval, A. B.; Hummelen, J. C. *J. Phys. Chem. A* **2005**, *109*, 5266–5274. (b) Theander, M.; Yartsev, A.; Zigmantas, D.; Sundstrom, V.; Mamm, W.; Andersson, M. R.; Inganäs, O. *Phys. Rev. B: Condens. Matter* **2000**, *61*, 12957–12963.
- (4) (a) Chirvase, D.; Parisi, J.; Hummelen, J. C.; Dyakonov, V. *Nanotechnology* **2004**, *15*, 1317–1323. (b) Savenije, T. J.; Kroeze, J. E.; Yang, X. N.; Loos, J. *Adv. Funct. Mater.* **2005**, *15*, 1260–1266.
- (5) Sivula, K.; Ball, Z. T.; Watanabe, N.; Fréchet, J. M. J. *Adv. Mater.* **2006**, *18*, 206–210.
- (6) Poly(3-hexylthiophene-2,5-diyl) from Rieke Metals, Inc. Our analysis confirms the advertised RR = 90–93% DCB GCP:  $M_n$  = 31 kDa, PDI = 2.0.
- (7) (a) Zen, A.; Pflaum, J.; Hirschmann, S.; Zhuang, W.; Jaiser, F.; Asawapirom, U.; Rabe, J. P.; Scherf, U.; Neher, D. *Adv. Funct. Mater.* **2004**, *14*, 757–764. (b) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J. S.; Fréchet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312–3319.
- (8) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Fréchet, J. M. J. *Appl. Phys. Lett.* **2005**, *86*, 122110.
- (9) (a) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685–688. (b) Pandey, S. S.; Takashima, W.; Nagamatsu, S.; Endo, T.; Rikukawa, M.; Kaneto, K. *Jpn. J. Appl. Phys., Part 2* **2000**, *39*, L94–L97.
- (10) Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. *Chem. Mater.* **2005**, *17*, 2175–2180.
- (11) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197–203.
- (12) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233–244.
- (13) (a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250–253. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.
- (14) Liu, J.; McCullough, R. D. *Macromolecules* **2002**, *35*, 9882–9889.

JA064434R